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see 37 CFR 51)

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INTERNATIONAL APPLICATION NO.

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16 February 2000

PRIORITY DATE CLAIMED

22 February 1999

TITLE OF INVENTION

AGGLOMERATED ZEOLITIC ADSORBENTS, METHOD FOR OBTAINING SAME AND USES
THEREOF

APPLICANT(S) FOR DO/EO/US

Dominique Plee, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith.
 - b. ☐ has been transmitted by the International Bureau (see accompanying PCT Form 308).
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
 - a. International application (PCT Publication No. WO 00/50166)
 - b. PCT Request (PCT/RO/101)
 - c. Form PCT/IPEA/416 and PCT/IPEA/409 (International Preliminary Examination Report)

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JCS Rec'd POT/PTO 22 AUG 2001

Atty. Dkt. No.
33808F156

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Dominique Plee, et al.

U.S. Serial No.: To Be Assigned

Group Art Unit: To Be Assigned

Filed: : August 22, 2001 (Herewith)

Examiner: To Be Assigned

For : Agglomerated Zeolitic Adsorbents, Method for Obtaining Same and Uses Thereof

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Prior to or concurrent with calculation of the filing fees, please amend this application as follows.

IN THE SPECIFICATION:

On page 1, please delete the paragraph heading "PRIOR ART" and insert the heading "Background of the Invention;

Applicants have attached to this Amendment a document entitled "Amended Specification." Please insert the indicated paragraph at the end of the present specification (page 13, line 14).

IN THE CLAIMS:

Applicants have attached to this Amendment documents entitled "Amended Claims" and "'Marked-up' Copy of the Previous Claims". Please replace present claims 1-8 and 12-17 in this application with amended claims 1-8 and 12-17 shown in the document entitled "Amended

Claims". Please also add new claim 18 which is shown in the document entitled "Amended Claims".

IN THE ABSTRACT:

Please reformat the Abstract to read as one paragraph instead of three.

REMARKS

Entry and consideration of this Preliminary Amendment are respectfully requested prior to or concurrent with calculation of the filing fees. This Preliminary Amendment is being filed to correct improper multiple dependencies. As so amended, the claims are submitted as appearing in proper multiple dependent form.

Examination on the merits is awaited.

AUTHORIZATION

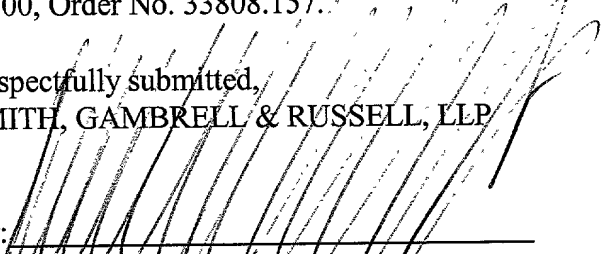
No additional fee is believed to be necessary.

The Commissioner is hereby authorized to charge any additional fees, which may be required for this amendment, or credit any overpayment to Deposit Account No. 02-4300, Order No. 33808.157.

In the event that an extension of time is required, or which may be required in addition to that requested in a petition for an extension of time, the Commissioner is requested to grant a petition for that extension of time which is required to make this response timely and is hereby

authorized to charge any fee for such an extension of time or credit any overpayment for an extension of time to Deposit Account No. 02-4300, Order No. 33808.157.

Respectfully submitted,
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MARKED UP COPY OF THE PREVIOUS CLAIMS

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1. Agglomerated zeolitic adsorbents [based on] comprising zeolite X with an Si/Al ratio such that $1.15 < \text{Si/Al} \leq 1.5$, at least 90% of the exchangeable cationic sites of the zeolite X of which are occupied either by barium ions alone or by barium ions and potassium ions, it being possible for the exchangeable sites occupied by potassium to represent up to 1/3 of the exchangeable sites occupied by barium + potassium wherein [(the possible remainder generally being provided by alkali metal or alkaline earth metal ions other than barium)] and an inert binder, [characterized in that] the Dubinin volume of [the-]said adsorbents measured by nitrogen adsorption at 77°K after degassing under vacuum at 300°C for 16 h, is greater than or equal to 0.240 cm³/g.
2. Adsorbents according to Claim 1, wherein [whose] Dubinin volume is ,greater than or equal to 0.245 cm³/g.
3. Adsorbents according to Claim 1 [or 2], wherein the overall degree of exchange of which with regard to barium alone or with regard to barium + potassium is greater than or equal to 95%.
4. Adsorbents according to [Claims 1 to 3] Claim 1, wherein the loss on ignition of which, measured at 900°C, is between 4.0 and 7.7% [and preferably between 5.2 and 7.7%].
5. Process for producing the adsorbents as defined in [any one of claims 1 to 4] Claim 1, comprising the following stages:
 - a) agglomerating zeolite X powder with a binder comprising at least 80% by weight of clay which can be converted to zeolite and shaping, then drying and calcining,
 - b) zeolitization of the binder by the action of an alkaline solution,
 - c) replacement of at least 90% of the exchangeable sites of the zeolite X by barium, followed by washing and drying the product thus treated,
 - d) optionally replacement of at most 33% of the exchangeable sites of the zeolite X by potassium, followed by washing and drying the product thus treated,
 - e) activation,
 [it being possible for the] optionally exchange with potassium (stage d)[)] to be carried out before or after the exchange with barium (stage c)[)].
6. Process for producing adsorbents according to Claim 5, [characterized in that] wherein the activation in stage e) is a thermal activation carried out at a temperature of 200 to 300°C.

7. Process for producing adsorbents comprising a binder which can be converted to zeolite according to Claim 5, wherein [or 6, characterized] in that the alkaline solution of stage b)[)] has a concentration of at least 0.5M.
8. Process for the recovery of para-xylene from C₈ aromatic isomer fractions in the liquid phase by adsorption of the para-xylene by [means of] an adsorbent according to [any one of Claims 1 to 4] Claim 1 in the presence of a desorbent.
12. Process for the recovery of para-xylene from C₈ aromatic isomer fractions in the gas phase by adsorption of the para-xylene by [means of] an adsorbent according to [any one of Claims 1 to 4] Claim 1 in the presence of a desorbent.
13. Process for the recovery of para-xylene according to [any one of Claims 8 to 12] Claim 8, [in which] wherein process the desorbent is toluene or para-diethylbenzene.
14. Process for the separation of sugars employing an adsorbent according to [any one of Claims 1 to 4] Claim 1.
15. Process for the separation of polyhydric alcohols employing an adsorbent according to [any one of Claims 1 to 4] Claim 1.
16. Process for the separation of substituted toluene isomers, [such as] including nitrotoluene, diethyltoluene or toluenediamine, employing an adsorbent according to [any one of Claims 1 to 4] Claim 1.
17. Process for the separation of cresols employing an adsorbent according to [any one of Claims 1 to 4] Claim 1.

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AMENDED CLAIMS

1. Agglomerated zeolitic adsorbents comprising zeolite X with an Si/Al ratio such that $1.15 < \text{Si/Al} \leq 1.5$, at least 90% of the exchangeable cationic sites of the zeolite X of which are occupied either by barium ions alone or by barium ions and potassium ions, it being possible for the exchangeable sites occupied by potassium to represent up to 1/3 of the exchangeable sites occupied by barium + potassium wherein the possible remainder generally being provided by alkali metal or alkaline earth metal ions other than barium and an inert binder, the Dubinin volume of said adsorbents measured by nitrogen adsorption at 77°K after degassing under vacuum at 300°C for 16 h, is greater than or equal to 0.240 cm³/g.
2. Adsorbents according to Claim 1, wherein Dubinin volume is greater than or equal to 0.245 cm³/g.
3. Adsorbents according to Claim 1, wherein the overall degree of exchange of which with regard to barium alone or with regard to barium + potassium is greater than or equal to 95%.
4. Adsorbents according to Claim 1, wherein the loss on ignition of which, measured at 900°C, is between 4.0 and 7.7%.
5. Process for producing the adsorbents as defined in Claim 1, comprising the following stages:
 - a) agglomerating zeolite X powder with a binder comprising at least 80% by weight of clay which can be converted to zeolite and shaping, then drying and calcining,
 - b) zeolitization of the binder by the action of an alkaline solution,
 - c) replacement of at least 90% of the exchangeable sites of the zeolite X by barium, followed by washing and drying the product thus treated,
 - d) optionally replacement of at most 33% of the exchangeable sites of the zeolite X by potassium, followed by washing and drying the product thus treated,
 - e) activation,
 optionally exchange with potassium (stage d) to be carried out before or after the exchange with barium (stage c).
6. Process for producing adsorbents according to Claim 5, wherein the activation in stage e) is a thermal activation carried out at a temperature of 200 to 300°C.
7. Process for producing adsorbents comprising a binder which can be converted to zeolite according to Claim 5, wherein in that the alkaline solution of stage b) has a concentration of at least 0.5M.

8. Process for the recovery of para-xylene from C₈ aromatic isomer fractions in the liquid phase by adsorption of the para-xylene by an adsorbent according to Claim 1 in the presence of a desorbent.
12. Process for the recovery of para-xylene from C₈ aromatic isomer fractions in the gas phase by adsorption of the para-xylene by an adsorbent according to Claim 1 in the presence of a desorbent.
13. Process for the recovery of para-xylene according to Claim 8, wherein process the desorbent is toluene or para-diethylbenzene.
14. Process for the separation of sugars employing an adsorbent according to Claim 1.
15. Process for the separation of polyhydric alcohols employing an adsorbent according to Claim 1.
16. Process for the separation of substituted toluene isomers, including nitrotoluene, diethyltoluene or toluenediamine, employing an adsorbent according to Claim 1.
17. Process for the separation of cresols employing an adsorbent according to Claim 1.
18. (New) Adsorbents according to Claim 4, wherein the loss on ignition is between 5.2 and 7.7%.

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AMENDED SPECIFICATION

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Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims. The foregoing references are hereby incorporated by reference.

AGGLOMERATED ZEOLITIC ADSORBENTS, THEIR PROCESS OF
PREPARATION AND THEIR USES

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TECHNICAL FIELD

The field of the invention is that of agglomerated zeolitic adsorbents based on zeolite X exchanged with barium or based on zeolite X exchanged with barium and with potassium.

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PRIOR ART

The prior art has recognized that adsorbents composed of zeolites X or Y exchanged by means of ions such as barium, potassium or strontium, alone or as a mixture, are effective in selectively adsorbing para-xylene in a mixture comprising at least one other C₈ aromatic isomer. Patents US 3,558,730, US 3,558,732, US 3,626,020 and US 3,663,638 disclose adsorbents comprising aluminosilicates exchanged by barium and potassium which efficiently separate para-xylene from a mixture of C₈ aromatic isomers.

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US 3,878,127 discloses a method for the preparation of adsorbents intended for the separation of xylenes, which consists in treating, in sodium hydroxide solution under hot conditions, agglomerates (zeolite X + binder) with an Na₂O/Al₂O₃ ratio of rigorously less than 0.7, in order to replace the exchangeable cations of the zeolite (such as protons or cations from Group IIA) with sodium prior to a barium or barium + potassium exchange, the preliminary exchange with sodium allowing a larger amount of barium or barium + potassium ions to be added to the zeolitic structure.

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These adsorbents may be used as adsorption agents in liquid-phase processes, preferably of simulated countercurrent type, similar to those disclosed in US 2,985,589, which apply, inter alia, to C₈ aromatic fractions resulting, for example, from processes for the dialkylation of benzene in gas-phase processes.

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Barium-exchanged zeolites X have numerous other applications as adsorption agents, among which may be mentioned:

* the separation of sugars, see, for example, EP 115,631 or EP 115,068,

* the separation of polyhydric alcohols (EP 137,063),

5 * the separation of substituted toluene isomers, US 4,642,397 (nitrotoluene), US 4,940,548 (diethyltoluene) or US 4,633,018 (toluenediamine),

* the separation of cresols (US 5,149,887).

10 In the above-listed references, the zeolitic adsorbents are provided in the form of a powder or in the form of agglomerates predominantly composed of zeolite having at least 15 to 20% by weight of inert binder and their Dubinin volume measured by nitrogen adsorption at 77°K after degassing under vacuum at 300°C for 16 h, is inferior
15 to 0.230 cm³/g.

As the synthesis of zeolites X is predominantly carried out by nucleation and crystallization of silicoaluminate gels, powders are obtained which are particularly difficult to employ on an industrial scale
20 (significant pressure drops when the powders are handled) and granular agglomerated forms are preferred. These agglomerates, whether in the form of blocks, balls or extrudates, are usually composed of a zeolite powder, which constitutes the active component, and of a binder intended
25 to ensure the cohesion of the crystals in the form of grains. This binder has no adsorbent property, its function being to confer on the grain sufficient mechanical strength to withstand the vibrations and movements to which it is subjected during its various uses. The agglomerates are
30 prepared by thickening zeolite powder with a clay paste, in proportions of the order of 80 to 85% of zeolite powder per 20 to 15% of binder, then shaping as balle, blocks or extrudates and heat treating at high temperature in order to bake the clay and reactivate the zeolite, it being
35 possible for exchange with barium to be carried out either before or after the agglomeration of the pulverulent zeolite with the binder. This results in zeolitic bodies with a particle size of a few millimetres which, if the binder is chosen and the granulation is carried out

according to the rules of the art, exhibit an array of satisfactory properties, in particular of porosity, of mechanical strength and of resistance to abrasion. However, the adsorption properties are obviously reduced in the ratio of active powder to the powder and its inert agglomeration binder.

Various means have been proposed for overcoming this disadvantage of the binder being inert with regard to the adsorbent performance, including the conversion of the binder, in all or part, to zeolite. This operation is usually carried out when binders of the kaolinite family, precalcined at temperatures of between 500°C and 700°C, are used. An alternative form consists in moulding kaolin grains and in converting them to zeolite: its principle is set out in "Zeolite Molecular Sieves" by D.W. Breck, John Wiley and Sons, New York. This technology has been applied with success to the production of grains of zeolite A or X which are composed of up to 95% by weight of the zeolite itself and of a residue of unconverted binder (see, to this end, US 3,119,660), the addition of a source of silica being recommended when it is desired to obtain a zeolite X ("Zeolite Molecule Sieves", Breck, p. 320).

Flank et al. show, in US 4,818,508, that it is possible to prepare agglomerates based on zeolite A, X or Y by digestion of reactive clay preforms (obtained by heat treatment of unreactive clay, such as halloysite or kaolinite, at least 50% by weight of which exists in the form of particles with a particle size of between 1.5 and 15 µm, preferably in the presence of a pore-forming agent) with an alkali metal oxide. The examples relating to the synthesis of agglomerates based on zeolite X show that it is necessary to add a source of silica, which is not the case when preparing agglomerates based on zeolite A.

JP-05163015 (Tosoh Corp.) teaches that it is possible to form grains of zeolite X with a low Si/Al ratio of less than 1.25 by mixing a zeolite LSX powder, the zeolite LSX having an Si/Al ratio of 1.25, with kaolin, potassium hydroxide, sodium hydroxide, carboxymethylcellulose. Shaping is carried out by

extrusion. The grains thus obtained are dried, calcined at 600°C for 2 hours and then immersed in a sodium hydroxide and potassium hydroxide solution at 40°C for 2 days.

These two documents teach that it is possible to prepare mechanically strong solids. Nevertheless, the associated processes are cumbersome and suffer either from the excessive reaction time or from the number of stages involved. Furthermore, it may be feared that the heat treatment as claimed in JP-05-163015, after the shaping stage, does not contribute to the amorphization of the grain and that the object of the caustic digestion which follows is to recrystallize it, which would explain the slowness of the process.

DESCRIPTION OF THE INVENTION

The subject-matter of the present invention is agglomerated zeolitic adsorbents based on zeolite X with an Si/Al ratio such that $1.15 < \text{Si/Al} \leq 1.5$, at least 90% of the exchangeable cationic sites of the zeolite X of which are occupied either by barium ions alone or by barium ions and potassium ions, it being possible for the exchangeable sites occupied by potassium to represent up to 1/3 of the exchangeable sites occupied by barium + potassium (the possible remainder generally being provided by alkali metal or alkaline earth metal ions other than barium (and potassium)) and an inert binder, characterized in that their Dubinin volume measured by nitrogen adsorption at 77°K after degassing under vacuum at 300°C for 16 hours, is greater than or equal to 0.240 cm³/g, preferably greater than or equal to 0.245 cm³/g.

The subject-matter of the present invention is also a process for the preparation of these agglomerates which comprises the following stages:

- a) agglomerating zeolite X powder with a binder comprising at least 80% by weight of clay which can be converted to zeolite and shaping, then drying and calcining,

- b) zeolitization of binder by the action of an alkaline solution,

- c) replacement of at least 90% of the exchangeable sites of the zeolite X by barium, followed by washing and drying the product thus treated,

5 - d) optionally replacement of at most 33% of the exchangeable sites of the zeolite X by potassium, followed by washing and drying the product thus treated,

- e) activation.

10 The agglomerating and the shaping (stage a)) can be carried out according to any technique known to a person skilled in the art, such as extrusion, compacting or agglomerating. The agglomeration binder employed in stage a) comprises at least 80% by weight of clay which can be converted to zeolite and can also comprise other inorganic binders, such as bentonite or attapulgite, and additives
15 intended, for example, to facilitate agglomeration and improve the hardening of the agglomerates formed.

The clay which can be converted to zeolite belongs to the kaolinite, halloysite, nacrite or dickite family. Use is generally made of kaolin. The calcination which
20 follows the drying is carried out at a temperature generally of between 500 and 600°C.

The zeolitization of the binder (stage b)) is carried out by immersion of the agglomerate in alkaline liquor, for example sodium hydroxide solution or a mixture
25 of sodium hydroxide solution and potassium hydroxide solution, the concentration of which is preferably greater than 0.5M. The zeolitization is preferably carried out under hot conditions, processing at a higher temperature than ambient temperature, typically at temperatures of the
30 order of 80-100°C, improving the kinetics of the process and reducing the immersion times. Zeolitizations of at least 50% of the binder are thus easily obtained. Washing with water, followed by drying, are subsequently carried out.

35 The exchange with barium of the cations of the zeolite (stage c)) is carried out by bringing the agglomerates resulting from stage b) (or d)) into contact with a barium salt, such as BaCl_2 , in aqueous solution at a temperature of between ambient temperature and 100°C and preferably of between 80 and 100°C. In order to quickly

obtain a high degree of exchange of barium, i.e. greater than 90%, it is preferable to carry out the exchange with a large excess of barium with respect to the cations of the zeolite which it is desired to exchange, typically such that the ratio $\text{BaO}/\text{Al}_2\text{O}_3$ is of the order of 10 to 12, successive exchanges being carried out so as to achieve the minimum targeted degree of exchange of at least 90% and preferably of at least 95%. Throughout the text, the degrees of exchange are calculated in equivalents and not in molarity.

The optional exchange with potassium (stage d)) can be carried out before or after the exchange with barium (stage c)); it is also possible to agglomerate zeolite X powder already comprising potassium ions.

The activation (stage e)) is the final stage in the preparation of the adsorbents according to the invention. The aim of the activation is to fix the water content, more simply the loss on ignition, of the adsorbent within optimum limits. The activation is generally carried out by thermal activation, which is preferably carried out between 200 and 300°C.

The invention also relates to the uses of the zeolitic adsorbents described above as adsorption agents capable of advantageously replacing the adsorption agents described in the literature based on zeolite X exchanged with barium or based on zeolite X exchanged with barium and potassium, in particular in the uses listed below:

- * the separation of C_8 aromatic isomers, in particular xylenes,

- * the separation of sugars,
- * the separation of polyhydric alcohols,
- * the separation of substituted toluene isomers, such as nitrotoluene, diethyltoluene or toluenediamine,
- * the separation of cresols.

The invention relates in particular to an improvement in the process for the recovery of para-xylene from C_8 aromatic isomer fractions which consists in using, as adsorption agent for p-xylene, a zeolitic adsorbent

according to the invention employed in liquid-phase processes but also gas-phase processes.

The desired product can thus be separated by (batch) preparative adsorption liquid chromatography, advantageously in a simulated moving bed, that is to say under simulated countercurrent conditions or under simulated cocurrent conditions, more particularly under simulated countercurrent conditions.

The operating conditions of an industrial adsorption unit of simulated countercurrent type are generally as follows:

number of beds	6 to 30
number of zones	at least 4
temperature	100 to 250°C
preferably	150 to 190°C
pressure	0.2 to 3 MPa
ratio of the desorbent to feedstock flowrates	1 to 2.5
(for example, 1.4 to 1.8 for a single adsorption unit (stand alone) and 1.1 to 1.4 for an adsorption unit combined with a crystallization unit)	
degree of recycling	3.5 to 12, preferably 4 to 6

Reference may be made to Patents US 2,985,589, US 5,284,992 and US 5,629,467.

The operating conditions of a simulated cocurrent industrial adsorption unit are generally the same as those operating under simulated countercurrent conditions, with the exception of the degree of recycling, which is generally between 0.8 and 7. Reference may be made to Patents US 4,402,832 and US 4,498,991.

The desorption solvent can be a desorbent with a boiling point lower than that of the feedstock, such as toluene, but also a desorbent with a boiling point greater than that of the feedstock, such as para-diethylbenzene (PDEB).

The selectivity of the adsorbents according to the invention for the adsorption of p-xylene present in C₈ aromatic fractions is optimum when their loss on ignition, measured at 900°C, is generally between 4.0 and 7.7% and preferably between 5.2 and 7.7%. Water and a small amount of carbon dioxide are included in the loss on ignition.

The following examples illustrate the invention.

EXAMPLES

These examples involve the measurement or the assessment of certain quantities characteristic of the adsorbents of the invention.

To assess the selectivity presented by the adsorbent of a process for the separation of para-xylene, a test is applied to it which allows the measurement of its separating power between para-xylene (PX) and its C₈ aromatic isomers (MX, OX), as well as between para-xylene and ethylbenzene (EB), which is important because some fractions may be rich in ethylbenzene but may not be rich in other C₈ isomers, and also between para-xylene and the desorbent, because it is just as important to have available a low PX/desorbent selectivity, a condition for the desorption to be efficient.

The test consists in immersing an adsorbent (17 g), thermally activated beforehand and cooled with the exclusion of air, in 80 g of a mixture of aromatics dissolved in 2,2,4-trimethylpentane.

The exact composition of the mixture is as follows:

	PX	2%
	MX	2%
30	OX	2%
	EB	2%
	toluene (desorbent)	2%
	2,2,4-trimethylpentane	the remainder

The mixture is heated in an autoclave at 150°C for 4 hours, a time sufficient to provide for adsorption equilibrium. A portion of the liquid is then withdrawn, condensed at -30°C and analysed by gas chromatography. It is then possible to work out the concentrations in the adsorbed phase and in the non-adsorbed phase and to express

the amount of para-xylene adsorbed and the selectivities for para-xylene with respect to the other aromatics and to the desorbent. The 2,2,4-trimethylpentane does not interfere with these results, not being adsorbed to any great extent. For Examples 1 and 2 hereinbelow, the desorbent employed is toluene.

The selectivity of the adsorbent thus prepared is measured according to the test described hereinbelow:

The selectivity $Sel(B/A)$ of an adsorbent for a compound (B) with respect to a compound (A) is defined as the ratio of the concentrations of the compounds in the adsorbed phase divided by the ratio of the concentrations of the compounds in the non-adsorbed phase at equilibrium.

The equation of the selectivity is as follows:

$$Sel(B/A) = \frac{(B)_z / (A)_z}{(B)_s / (A)_s}$$

where $(B)_z$ and $(B)_s$ represent the concentrations of B in the zeolite and the solution respectively,

where $(A)_z$ and $(A)_s$ represent the concentrations of A in the zeolite and the solution.

EXAMPLE 1: control adsorbent

An industrial zeolite NaX, with an Si/Al ratio of 1.25 and an Na/Al ratio of 1, is agglomerated by intimately mixing 850 g of zeolite X powder (expressed as calcined equivalent), 150 g of Charentes kaolinite (expressed as calcined equivalent) and 6 g of carboxymethylcellulose (retention adjuvant intended to retain the water during the extrusion operation) with the appropriate amount of water for the extrusion. The extrudate is dried, crushed, so as to recover grains with an equivalent diameter equal to 0.7 mm, and then calcined at 550°C under a stream of nitrogen for 2 h. Its toluene adsorption capacity, determined at 25°C and under a partial pressure of 0.5, is 20.2%; it is interpreted as a micropore volume of $20.2/0.86 = 0.235 \text{ cm}^3/\text{g}$ (in the calculation of the pore volume, the relative density of the liquid phase is regarded as being identical

to the relative density of the adsorbed toluene, that is to say 0.86).

This granule is exchanged by means of a 0.5M barium chloride solution at 95°C in 4 stages. In each stage, the ratio of volume of solution to mass of solid is 20 ml/g and the exchange is continued for 4 hours each time. Between each exchange, the solid is washed several times, so as to free it from the excess salt. It is subsequently activated at a temperature of 250°C for 2 h under a stream of nitrogen.

The degree of exchange with regard to barium is 97%. The toluene adsorption capacity is 14.8%, which equates to a micropore volume of 0.17 cm³/g. The loss on ignition, an important quantity as it gives an estimation of residual water present on the adsorbent, is also measured: a loss on ignition of 4.5% is recorded here. The micropore volume, measured according to the Dubinin method by nitrogen adsorption at 77°K after degassing under vacuum at 300°C for 16 h, is 0.22 cm³/g.

Application of the selectivity test described above leads to the following results:

Isomers	Selectivity
PX/OX	2.25
PX/MX	2.12
PX/EB	1.77
PX/Tol	1.52

The amount of para-xylene adsorbed is equal to 0.054 cm³/g.

EXAMPLE 2 : adsorbent according to the invention

An industrial zeolite NaX, with an Si/Al ratio of 1.25 and an Na/Al ratio of 1, is agglomerated by intimately mixing 800 g of zeolite X powder (expressed as calcined equivalent), 150 g of kaolin (expressed as calcined equivalent), 56 g of colloidal silica, sold by the company CECA under the tradename Cecasol®30 (and comprising 30% by weight of SiO₂ and 0.5% of Na₂O), and 6 g of carboxymethylcellulose with the appropriate amount of water for the extrusion. The extrudate is dried, crushed, so as

to recover grains with an equivalent diameter equal to 0.7 mm, and then calcined at 550°C under a stream of nitrogen for 2 h. Its toluene adsorption capacity, determined at 25°C and under a partial pressure of 0.5, is 19.8%; it is
5 interpreted as corresponding to a micropore volume of 0.23 cm³/g from the relative density of the toluene adsorbed, estimated from that for the liquid toluene.

200 g of granules thus obtained are placed in a glass reactor equipped with a jacket, which jacket is
10 regulated at a temperature of 100 ± 1°C, 1.5 l of an aqueous sodium hydroxide solution with a concentration of 100 g/l are then added and the reaction mixture is left stirring for 3 h. The granules are subsequently washed in 3 successive washing operations with water and then the
15 reactor is emptied. The effectiveness of the washing is confirmed by measuring the final pH of the aqueous wash liquors, which must be between 10 and 10.5.

The toluene adsorption capacity of the granules thus obtained is determined under the same conditions as
20 those described in Example 1: 22.5%, corresponding to a micropore volume of 0.26 cm³/g, that is to say a gain in crystallinity of approximately 13% with respect to the granules of Example 1.

A barium exchange is subsequently carried out under
25 operating conditions identical to those for Example 1, with the exception of the concentration of the BaCl₂ solution, which is 0.6M, followed by washing, then by drying at 80°C for 2 h and, finally, by activation at 250°C for 2 h under a stream of nitrogen.

30 The degree of exchange with regard to barium of this adsorbent is 97.4%, its toluene adsorption capacity is 16.2% and its loss on ignition is 5.2%. The micropore volume, measured according to the Dubinin method by nitrogen adsorption at 77°K after degassing under vacuum at
35 300°C for 16 h, is 0.244 cm³/g.

Application of the selectivity test described above leads to similar results to those obtained for the control adsorbent of Example 1; the amount of para-xylene adsorbed is equal to 0.06 cm³/g.

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EXAMPLE 3 (comparative)

5 A continuous liquid chromatography pilot unit is constructed comprising 24 columns in series with a length of 1 m and diameter of 1 cm, circulation between the 24th column and the 1st taking place by means of a recycling pump. Each of these columns is charged with the adsorbent prepared in Example 1 and the entire unit (columns + pipework + distribution valves) is placed in an oven at 10 150°C.

15 According to the principle of simulated countercurrent chromatography, the injection of solvent, the withdrawal of extract, the injection of the feedstock and the withdrawal of the raffinate are advanced by 3 columns every 6 min cocurrentwise to the circulation of liquid: 6 columns (2 beds) are found between the injection of solvent and withdrawal of extract, 9 columns (3 beds) are found between the withdrawal of extract and injection of feedstock, three columns (1 bed) are found between the 20 injection of feedstock and the withdrawal of raffinate and the final 6 columns are situated between the withdrawal of raffinate and the injection of solvent.

25 Continuous injection is carried out (expressed under ambient conditions) of 7.3 cm³/min of toluene and 5 cm³/min of a feedstock composed of 21% by weight of para-xylene, 17% of ethylbenzene, 44% of meta-xylene and 18% of ortho-xylene.

Continuous withdrawal is carried out of 5.4 cm³/min of extract and 6.74 cm³/min of raffinate.

30 During the first 2 periods of a cycle, the recycling pump delivers (at ambient temperature) 38.7 cm³/min; it delivers 45.5 cm³/min during the 3rd period, 40.5 cm³/min during the following 3 periods and 45.9 cm³/min during the final 2 periods. para-Xylene is obtained with a 35 purity of 92.2% and with a degree of recovery of 98.1%. The temperature is 150°C and the pressure decreases from 30 to 5 bar. It is calculated that the productivity of the adsorbent is 0.034 m³ of para-xylene adsorbed per m³ of adsorbent per hour.

EXAMPLE 4 (according to the invention)

The pilot unit described in Example 3 is now operated with the adsorbent prepared in Example 2. It is
5 observed that it is possible to obtain the same purity of para-xylene while increasing the flow rate of the feedstock entering the pilot unit up to $5.5 \text{ cm}^3/\text{min}$ (i.e. an increase of 10%).

For this feedstock flow rate, the amount of
10 desorbent introduced corresponds to a flow rate of $7.92 \text{ cm}^3/\text{min}$, the permutation time is 5.4 min and the productivity of adsorbent is 0.0374 m^3 of para-xylene adsorbed per m^3 of adsorbent per hour.

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CLAIMS

1. Agglomerated zeolitic adsorbents based on zeolite X with an Si/Al ratio such that $1.15 < \text{Si/Al} \leq 1.5$, at least 90% of the exchangeable cationic sites of the zeolite X of which are occupied either by barium ions alone or by barium ions and potassium ions, it being possible for the exchangeable sites occupied by potassium to represent up to 1/3 of the exchangeable sites occupied by barium + potassium (the possible remainder generally being provided by alkali metal or alkaline earth metal ions other than barium) and an inert binder, characterized in that the Dubinin volume of the-said adsorbents measured by nitrogen adsorption at 77°K after degassing under vacuum at 300°C for 16 h, is greater than or equal to 0.240 cm³/g.
2. Adsorbents according to Claim 1 whose Dubinin volume is ,greater than or equal to 0.245 cm³/g.
3. Adsorbents according to Claim 1 or 2, the overall degree of exchange of which with regard to barium alone or with regard to barium + potassium is greater than or equal to 95%.
4. Adsorbents according to Claims 1 to 3, the loss on ignition of which, measured at 900°C, is between 4.0 and 7.7% and preferably between 5.2 and 7.7%.
5. Process for producing the adsorbents as defined in any one of claims 1 to 4, comprising the following stages:
- a) agglomerating zeolite X powder with a binder comprising at least 80% by weight of clay which can be converted to zeolite and shaping, then drying and calcining,
 - b) zeolitization of the binder by the action of an alkaline solution,
 - c) replacement of at least 90% of the exchangeable sites of the zeolite X by barium, followed by washing and drying the product thus treated,
 - d) optionally replacement of at most 33% of the exchangeable sites of the zeolite X by potassium, followed by washing and drying the product thus treated,
 - e) activation,

it being possible for the optional exchange with potassium (stage d)) to be carried out before or after the exchange with barium (stage c)).

6. Process for producing adsorbents according to Claim 5, characterized in that the activation in stage e) is a thermal activation carried out at a temperature of 200 to 300°C.

7. Process for producing adsorbents comprising a binder which can be converted to zeolite according to Claim 5 or 6, characterized in that the alkaline solution of stage b)) has a concentration of at least 0.5M.

8. Process for the recovery of para-xylene from C₈ aromatic isomer fractions in the liquid phase by adsorption of the para-xylene by means of an adsorbent according to any one of Claims 1 to 4 in the presence of a desorbent.

9. Process for the recovery of para-xylene according to Claim 8 of simulated moving bed type.

10. Process for the recovery of para-xylene according to Claim 9 of simulated countercurrent type.

11. Process for the recovery of para-xylene according to Claim 9 of simulated cocurrent type.

12. Process for the recovery of para-xylene from C₈ aromatic isomer fractions in the gas phase by adsorption of the para-xylene by means of an adsorbent according to any one of Claims 1 to 4 in the presence of a desorbent.

13. Process for the recovery of para-xylene according to any one of Claims 8 to 12, in which process the desorbent is toluene or para-diethylbenzene.

14. Process for the separation of sugars employing an adsorbent according to any one of Claims 1 to 4.

15. Process for the separation of polyhydric alcohols employing an adsorbent according to any one of Claims 1 to 4.

16. Process for the separation of substituted toluene isomers, such as nitrotoluene, diethyltoluene or toluenediamine, employing an adsorbent according to any one of Claims 1 to 4.

17. Process for the separation of cresols employing an adsorbent according to any one of Claims 1 to 4.

Declaration and Power of Attorney United States Patent Application

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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **AGGLOMERATED ZEOLITIC ADSORBENTS, METHOD FOR OBTAINING SAME AND USES THEREOF**

(check one) ☐ is attached hereto.

☒ was filed as U.S. Application No. _____ on August 22, 2001 and (if applicable) was amended on even date.
☒ was filed as PCT International Application No. PCT/FR00/00382 on February 16, 2000
and (if applicable) was amended under PCT Article 34 on _____.

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.
I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or §365(b) of any foreign and PCT application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America listed in this Declaration. I have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application(s) on which priority is claimed:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)
99/02151	France	2/22/99	Yes

I hereby claim the benefit under Title 35, United States Code, §120 or §365(c) of any United States application and PCT international application designating the United States of America listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

The duty is acknowledged for the Preliminary Amendment, which is hereby incorporated by reference as part of the original disclosure.

I hereby claim priority benefits under Title 35 United States Code §119(e) of any U.S. provisional application(s) listed below:

U.S. Provisional Application No.	Filing Date

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Robert G. Weilacher (20,531), Herbert M. Hanegan (25,682), Dale Lischer (28,438), Frederick F. Calvetti (28,557), J. Rodgers Lunsford, III (29,405), Michael A. Makuch (32,263), Dennis C. Rodgers (32,936), Michael K. Carrier (42,391), Eric J. Hanson (44,738), Patrick R. Delaney (45,338), and Brandon S. Boss (46,567).

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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